

COATINGS

UDC 620.17:669.24

STRUCTURAL TRANSFORMATIONS IN HEAT-RESISTANT CERAMIC COATINGS AND SURFACE LAYERS OF THE ALLOY ZhS6U

N. I. Afanas'ev¹ and V. D. Kitler¹Translated from *Steklo i Keramika*, No. 2, pp. 31 – 33, February, 2009.

The change in the structure and phase and chemical compositions of bilayer heat-resistance coatings and surface layers of the alloy ZhC6U under a coating in the process of high-temperature annealing and creep in investigated. Deposition of an additional ceramic coating consisting of 40% Y_2O_3 , 40% ZrO_2 , 10% Cr_2O_3 , and 10% Al_2O_3 increases the creep resistance of the heat-resistant alloy.

One of the main problems of the modern materials science of heat-resistant alloys is increasing their resistance to the environment. One way to solve this problem is to use protective coatings.

The chemical composition and structure of a coating, such as an alloy, change substantially at high temperatures because of diffusion processes. The diffusion of the components of the protection system into the alloy decreases the strength of the alloy as well as the creep resistance, and the diffusion of the component of the alloy in the coating decreases the heat-resistance of the alloy. In addition, impurity diffusion flows along the interior interfaces in themselves affect recrystallization, creep, slip along grain boundaries, and pore formation [1].

The study of the degradation of the structure of a coating is of great importance for developing optimal protective systems and methods for depositing them. It is also of interest to study the effect of coatings on the mechanical properties of heat-resistant alloys.

Heat-resistant coatings based on the system $Ni(Co) – Cr – Al – Y$ are widely used to protect complexly alloyed heat-resistant alloys based on nickel [2]. Research has shown that such coatings do not completely prevent oxygen penetration to the surface of an alloy [3]. This results in internal oxidation of the alloy under the coating and degradation of its protective properties.

In the present work, bilayer coatings were used to prevent internal oxidation. The first (inner) layer consisting of a

nickel-based alloy containing 20%² Cr, 13% Al, and 0.5% Y was deposited on the prepared surface of the ZhS6U alloy. The second (outer) layer consisted of a ceramic (40% Y_2O_3 , 40% ZrO_2 , 10% Cr_2O_3 , 10% Al_2O_3). The inner coating was about 100 μm thick, and the outer coating about 50 μm thick. The coatings were obtained by high-energy vacuum plasma technology [4]. The mechanical tensile and creep test were performed at temperature 1273 K in vacuum 1×10^{-3} Pa and in the air atmosphere. Flat samples with heads with a $2 \times 3 \times 20$ mm^3 working part were used. X-ray structural analysis, x-ray spectral microanalysis, and optical as well as electron microscopy were used to study the structural and chemical transformations in the surface layers of the alloy and in coating during annealing and creep.

Figure 1 shows the bilayer coating and the surface layer of the alloy ZhS6U after different annealing times in air at 1273 K. Prolonged annealing results in degradation of the structure of the ceramic coating. After annealing for 50 h the coating opens up; pores and microcracks form in it and destruction and separation of the coating are observed. After annealing for 80 h in air the ceramic coating completely burns up.

Scale appears on the surface of the ZhS6U alloy and to a lesser degree on the coating consisting of the nickel-based alloy; this scale loosens and detaches as the annealing time increases. After annealing for 100 h in air the nickel-based coating becomes 10 – 15% thinner but remains compact and retains its protective properties. Diffusion zones form between the coatings as well as between the inner coating and

¹ Tomsk Science Center of the Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia.

² Here and below unless otherwise stated — content by weight.

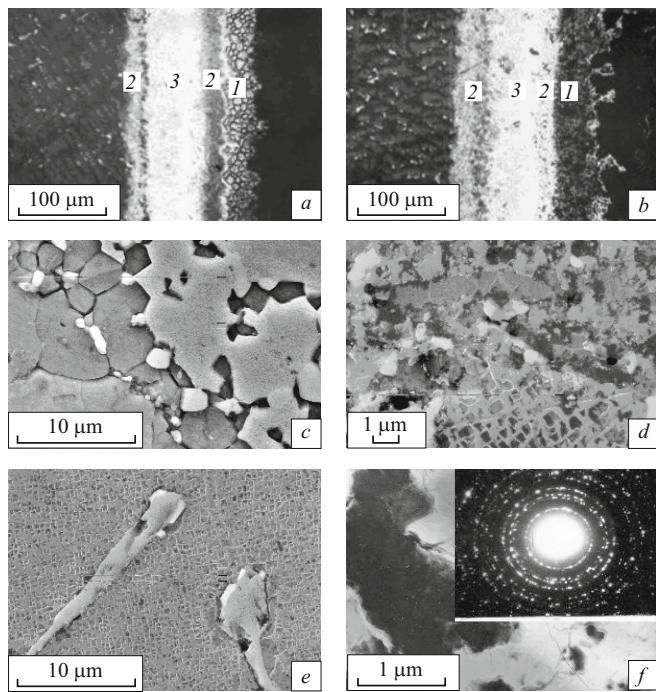


Fig. 1. Bilayer coating and surface layer of the alloy ZhS6U: *a* and *b*) structure of the bilayer coating after annealing for 4 and 50 h at 1273 K, *1*) ceramic coating, *2*) diffusion zones, *3*) coating consisting of a nickel-based alloy containing 20% Cr, 13% Al, 0.5% Y; *c*) grain structure of the ceramic coating after annealing for 4 h; *d*) structure between the nickel-based coating and the ZhS6U alloy; *e*) carbides and γ' phase in the alloy ZhS6U after annealing for 4 h; *f*) oxides in the alloy under the coating and electron-diffraction pattern.

the alloy (see Fig. 1). The dependence of the width of the diffusion zone on the annealing time is parabolic. The growth rate of the diffusion zone during creep is three to four times lower than during annealing without a load. This could be due to compression stresses arising in the transverse section of the sample during creep.

The ZhS6U alloy possesses a dendritic structure. The main hardening phases are γ' (Ni_3Al) and carbides (predominately) Cr_7C_3 . The volume fraction of the γ' phase is about 55%, and 0.1 – 0.3 μm particles have a cubic shape. Large particles of the γ' phase and eutectic γ'/γ up to 10 μm in size are encountered. No close-packed topological phases are observed in the alloy in any heat-treatment regime. The grain size in the alloy after 4 h of homogenizing annealing at 1273 K is 30 – 40 μm . The carbide particles are shaped like plates and rods up to 15 μm long and 5 μm thick. Coalescence of grains and phases in the alloy is observed during annealing and creep. After annealing for 50 h the grain size doubles, and the particles of the γ' phase reach 0.8 – 1.0 μm in size.

After deposition both coatings possess an ultra-fine-grain structure with 0.2 – 0.3 μm grains and phases. The grain structure in the indicated nickel-based coating exhibits

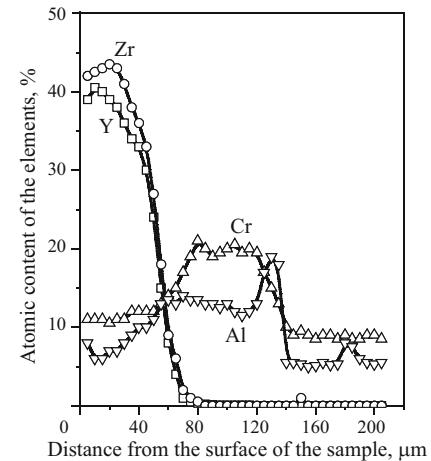


Fig. 2. Elemental content in coatings and the surface layer of the alloy ZhS6U versus depth.

higher thermal stability. Annealing for 4 h increases the average grain size in this coating to 1 μm and after 50 h to 2.2 μm . The average grain size in the ceramic coating with the indicated composition is 5 and 15 μm after the corresponding heat-treatments.

X-ray structural analysis showed NiAl , Ni_3Al , and free chromium in the first coating. These phases are characteristic for all the states studied, but the distribution of the relative intensity of the lines as a function of the heat treatment changes. The relative intensity of the x-ray lines decreases for the NiAl phase and increases for the Ni_3Al phase. The decrease of the amount of the Ni_3Al phase is due to the consumption of aluminum in the formation of Al_2O_3 and to the diffusion of aluminum into the alloy. The phases Y_2O_3 , Cr_2O_3 , ZrO_2 , and $\alpha\text{-Al}_2\text{O}_3$ were found in the ceramic coating.

Figure 2 shows the distribution of the alloying elements in coatings and near-surface layer of the alloy. An elevated content of aluminum and titanium is observed between the alloy and the coating. This could be due to diffusion of aluminum out of the coating into the alloy which decreases the volume fraction of the γ' phase and to the penetration of oxygen to the surface of the alloy with titanium oxides forming. Electron microscopy confirms the latter assumption.

In alloys with a single-layer coating, oxidation of the surface of the alloy under the coating starts after 5 – 10 h of annealing or creep in air at temperature 1273 K. In an alloy with a bilayer coating, the formation of oxides is delayed by 40 – 50 h. During this period of time, through pores appear in the ceramic coating and oxygen penetrates to the surface of the first coating and diffuses through it. Titanium and nickel oxides form on the surface of the alloy ZhS6U under the nickel-based coating. The structure of the oxides is shown in Fig. 1*f*.

The long-term ultimate strength of the alloy ZhS6U without a coating, with a single-layer coating, and a bilayer coating at 1273 K in vacuum after annealing for 100 h is, ne-

glecting the coating cross section, 170 MPa. At 1273 K the coatings possess low ultimate strength under an active load (3 – 5 MPa), so that taking account of the cross section of the coating the long-term strength of the samples decreases [5]. Testing in air under the same conditions decreases the time to failure of the samples to 50 h without a coating and to 80 h with a single-layer coating consisting of the nickel-based alloy. The difference between the times to failure in the test performed in air and in vacuum decreases as the sample size increases. This is due to the anomalous manifestation of the scale factor in long-duration tests under corrosion conditions. The deposition of an additional barrier coating based on a ceramic belonging to the system $Y_2O_3 - ZrO_2 - Cr_2O_3 - Al_2O_3$ increases the time to failure of the samples to 90 h.

This ceramic coating possesses a lower heat-resistance than a coating consisting of the nickel-based alloy. A 50 μm thick coating is completely destroyed over an annealing time of 80 h in air at 1273 K. In the course of annealing, intense growth of grains is observed in the ceramic coating, and loosening of the material with pores being formed occurs on the outer and inner interfaces. After annealing for 50 h at 1273 K, through pores appear along the grain boundaries,

and oxygen feely penetrates to the first coating. The nickel-based coating remains compact and retains its protective properties after undergoing annealing for 100 h in air.

The deposition of an additional ceramic coating increases by 10% the time to failure of the ZhS6U alloy samples in the process of high-temperature creep in air.

REFERENCES

1. Yu. R. Kolobov, R. Z. Valiev, G. P. Grabovetskaya, et al., *Grain-Boundary Diffusion and the Properties of Nanostructural Materials* [in Russian], Nauka, Novosibirsk (2001).
2. *Heat-Resistant Alloys for Gas Turbines* [in Russian], Metallurgiya (1981).
3. N. I. Afanas'ev, L. S. Bushnev, M. K. Kasymov, et al., "Effect of the heat-resistance coating on the degradation of the microstructure of the alloy ZhS6U," *Izv. Vyssh. Ucheb. Zaved., Ser. Fizika*, No. 12, 109 – 111 (1986).
4. *Surface Treatment and Reliability of Materials* [Russian translation], Mir, Moscow (1985).
5. N. I. Afanas'ev, L. S. Bushnev, S. A. Muboyadzhan, et al., "Structure and properties of heat-resistance coatings consisting of the alloy Ni – Cr – Al – Y," *Izv. Vyssh. Ucheb. Zaved., Ser. Fizika*, No. 12, 22 – 25 (1986).